



UNIVERSITI PUTRA MALAYSIA

**PREPARATION AND CHARACTERIZATION OF $\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$ (M =
P, AS, V) OXIDE ION CONDUCTORS**

LEE SIEW LING.

FSAS 2004 25

**PREPARATION AND CHARACTERIZATION OF
 $\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$ (M = P, As, V) OXIDE ION CONDUCTORS**

By

LEE SIEW LING

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

May 2004



for Bon and family with love



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement of the degree of Doctor of Philosophy

**PREPARATION AND CHARACTERIZATION OF
 $\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$ ($\text{M} = \text{P, As, V}$) OXIDE ION CONDUCTORS**

By

LEE SIEW LING

May 2004

Chairman: Professor Lee Chnoong Kheng Ph.D.

Faculty: Science and Environmental Studies

$\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$, $\text{M} = \text{P, As, V}$ systems and related materials were prepared by solid state reactions. The phase purity of the materials was determined by X-ray diffraction (XRD). Further characterization using ac impedance spectroscopy and differential thermal analysis (DTA) were carried out on single phase materials. Besides, inductively coupled plasma-atomic emission spectrometry (ICP-AES), density measurement, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), Fourier-transform infrared (FT-IR) spectroscopy and Raman spectroscopy were also performed on selected materials. The crystal system and space group of the single phase materials were determined.

Two narrow solid solution series were formed in $x\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$: $5.5 \leq x \leq 6$ and $7 \leq x \leq 7.25$. In DTA study, a phase transition was clearly seen in $\text{Bi}_7\text{PO}_{13}$ and $\text{Bi}_{29}\text{P}_4\text{O}_{53.5}$ at $\sim 860^\circ\text{C}$.

XRD shows that single phase materials were formed in $x\text{Bi}_2\text{O}_3\text{-As}_2\text{O}_5$ binary system when $x = 5, 5.5, 5.667, 5.75, 6$ and 7 . Among these, materials in the composition range of $5 \leq x \leq 6.25$ appeared to be solid solutions. Attempts to synthesize materials of composition of $x\text{Bi}_2\text{O}_3\text{-As}_2\text{O}_5$, $1 \leq x \leq 4$ were unsuccessful.

Single phase materials were formed in $x\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ binary system, $5 \leq x \leq 6$ and $x = 7$. A phase transition was observed in $\text{Bi}_{17}\text{V}_3\text{O}_{33}$ and $\text{Bi}_{23}\text{V}_4\text{O}_{44.5}$ at $\sim 180^\circ\text{C}$. However, its origin is unknown.

Materials of composition $x\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$, $5.5 \leq x \leq 6$ ($\text{M} = \text{P}$) and $5 \leq x \leq 6$ ($\text{M} = \text{As}, \text{V}$) are refined in triclinic symmetry with space group of $P-1$. Meanwhile, monoclinic symmetry was found in materials where $x = 7, 7.25$ ($\text{M} = \text{P}$) and $x = 7$ ($\text{M} = \text{As}, \text{V}$). The XRD and IR patterns of both series of $x\text{Bi}_2\text{O}_3\text{-As}_2\text{O}_5$, $5 \leq x \leq 6.25$ and $x\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$, $5.5 \leq x \leq 6$ solid solutions are very similar since these materials are isostructural. Generally, lattice parameters, volumes and densities of the materials in $x\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$ system, $\text{M} = \text{P}, \text{As}, \text{V}$ increased with the increase of Bi content.

A complete solid solution series was formed in the $\text{Bi}_{22}\text{P}_4\text{O}_{43}\text{-Bi}_{22}\text{As}_4\text{O}_{43}$, $\text{Bi}_{22}\text{P}_4\text{O}_{43}\text{-Bi}_{22}\text{V}_4\text{O}_{43}$, $\text{Bi}_{22}\text{As}_4\text{O}_{43}\text{-Bi}_{22}\text{V}_4\text{O}_{43}$, $\text{Bi}_{23}\text{P}_4\text{O}_{44.5}\text{-Bi}_{23}\text{As}_4\text{O}_{44.5}$, $\text{Bi}_{23}\text{P}_4\text{O}_{44.5}\text{-Bi}_{23}\text{V}_4\text{O}_{44.5}$, $\text{Bi}_{23}\text{As}_4\text{O}_{44.5}\text{-Bi}_{23}\text{V}_4\text{O}_{44.5}$, $\text{Bi}_{12}\text{P}_2\text{O}_{23}\text{-Bi}_{12}\text{As}_2\text{O}_{23}$, $\text{Bi}_{12}\text{P}_2\text{O}_{23}\text{-Bi}_{12}\text{V}_2\text{O}_{23}$, $\text{Bi}_{12}\text{As}_2\text{O}_{23}\text{-Bi}_{12}\text{V}_2\text{O}_{23}$ and $\text{Bi}_7\text{AsO}_{13}\text{-Bi}_7\text{VO}_{13}$ systems. In $\text{Bi}_7\text{PO}_{13}\text{-Bi}_7\text{AsO}_{13}$ and $\text{Bi}_7\text{PO}_{13}\text{-Bi}_7\text{VO}_{13}$ systems a two-phase region was seen. All the single phase materials studied above appeared to be oxide-ion conductors. Conductivity increased with increasing vanadium

content, followed by arsenic and phosphorus. Among the materials prepared, the highest conductivity is obtained in $\text{Bi}_{23}\text{V}_4\text{O}_{44.5}$ with a σ value of $1.34 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 300°C . In an attempt to optimize oxide ion conductivity, chemical doping using PbO , $\text{Sr}(\text{NO}_3)_2$, Al_2O_3 , Ga_2O_3 , La_2O_3 , Fe_2O_3 *etc.* was carried out in selected materials, resulting in the formation of limited solid solutions. These materials, however, exhibit conductivity slightly lower than that of the parent materials.

Ball milling process has been carried out in the preparation of $\text{Bi}_{23}\text{V}_4\text{O}_{44.5}$ and $\text{Bi}_{14}\text{PO}_8$ in addition to manual grinding prior to firing of the samples. In ball milling process, high-density, fine-grained powders with uniform grain-size distribution were obtained, resulting in an increase in conductivity and dielectric constants.

Sillenite compounds in the $\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ binary system with Bi:P ratios of 13:1 to 16:1 have been synthesized and found to be solid solutions. Substitution of P by V and As in the material where Bi:P = 14:1 results in partial and complete solid solutions, respectively. Enhancement in conductivity was observed in these solid solutions with V-doped materials exhibiting the highest conductivity. Substitution of P by elements such as Pb^{2+} , Sr^{2+} , Al^{3+} , Ga^{3+} , Fe^{3+} , Si^{4+} , Ge^{4+} , and Ti^{4+} leads to formation of limited solid solutions. Most of these materials have conductivity similar to or slightly higher than that of the parent compound. These materials appeared to be predominantly oxide ion conductors especially at temperatures above 800°C where $\gamma \rightarrow \delta'$ polymorphic transformation occurred.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**PENYEDIAAN DAN PENCIRIAN KONDUKTUR ION OKSIDA
 $\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$ (M = P, As, V)**

Oleh

LEE SIEW LING

Mei 2004

Pengerusi: Profesor Lee Chnoong Kheng, Ph.D.

Fakulti: Sains dan Pengajian Alam Sekitar

Sistem-sistem $\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$, M = P, As, V dan bahan-bahan berkaitan telah disediakan melalui tindak balas keadaan pepejal. Ketulenan fasa bahan tersebut dikenalpastikan dengan penggunaan pembelauan sinar-X (XRD). Pencirian lanjutan telah dijalankan ke atas sampel yang berfasa tunggal dengan menggunakan spektroskopi impedans arus ulang-alik dan penganalisa pembezaan terma (DTA). Di samping itu, analisis-analisis termasuk analisis plasma induktif pasangan-pemancaran pengatoman (ICP-AES), penyukatan ketumpatan, analisis termogravimetri (TGA), kalorimetri pembezaan imbasan (DSC), mikroskopi imbasan elektron (SEM), spektroskopi infra merah transformasi Fourier (FT-IR) dan spektroskopi Raman telah dijalankan ke atas sampel-sampel terpilih. Sistem hablur dan kumpulan ruangan bagi sample-sampel yang berfasa tunggal juga dikenalpastikan.

Larutan pepejal telah terbentuk dalam sistem $x\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$: $5.5 \leq x \leq 6$ dan $7 \leq x \leq 7.25$.

Dalam kajian DTA, suatu peralihan fasa didapati dalam $\text{Bi}_7\text{PO}_{13}$ dan $\text{Bi}_{29}\text{P}_4\text{O}_{53.5}$ pada $\sim 860^\circ\text{C}$.

XRD menunjukkan bahan berfasa tunggal telah terbentuk dalam sistem $\text{Bi}_2\text{O}_3\text{-As}_2\text{O}_5$ apabila $x = 5, 5.5, 5.667, 5.75, 6$ and 7 . Bahan-bahan dengan komposisi $5 \leq x \leq 6.25$ wujud sebagai pepejal larutan. Percubaan untuk menyintesis komposisi $x\text{Bi}_2\text{O}_3\text{-As}_2\text{O}_5$, $1 \leq x \leq 4$ telah mengalami kegagalan.

Bahan berfasa tunggal terbentuk dalam sistem $x\text{Bi}_2\text{O}_3 : \text{V}_2\text{O}_5$, $5 \leq x \leq 6$ dan $x = 7$. Suatu peralihan fasa telah didapati dalam $\text{Bi}_{17}\text{V}_3\text{O}_{33}$ dan $\text{Bi}_{23}\text{V}_4\text{O}_{44.5}$ pada $\sim 180^\circ\text{C}$. Tetapi, sifat asalnya tidak diketahui.

Sistem hablur bagi bahan-bahan berkomposisi $x\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$, $5.5 \leq x \leq 6$ ($\text{M} = \text{P}$) dan $5 \leq x \leq 6$ ($\text{M} = \text{As}, \text{V}$) adalah bersimetri triklinik dengan kumpulan ruangan $P-1$. Sementara, sistem hablur bersimetri monoklinik didapati apabila $x = 7, 7.25$ ($\text{M} = \text{P}$) dan $x = 7$ ($\text{M} = \text{As}, \text{V}$). Pola XRD dan IR bagi kedua-dua siri pepejal larutan $x\text{Bi}_2\text{O}_3\text{-As}_2\text{O}_5$, $5 \leq x \leq 6.25$ dan $x\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$, $5.5 \leq x \leq 6$ adalah mirip kerana mereka memiliki struktur yang serupa. Secara amnya, parameter kekisi, isipadu dan ketumpatan bahan-bahan dalam sistem $x\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$, $\text{M} = \text{P}, \text{As}, \text{V}$ meningkat dengan penambahan kandungan Bi.

Siri larutan pepejal yang lengkap terbentuk dalam sistem-sistem $\text{Bi}_{22}\text{P}_4\text{O}_{43}\text{-Bi}_{22}\text{As}_4\text{O}_{43}$, $\text{Bi}_{22}\text{P}_4\text{O}_{43}\text{-Bi}_{22}\text{V}_4\text{O}_{43}$, $\text{Bi}_{22}\text{As}_4\text{O}_{43}\text{-Bi}_{22}\text{V}_4\text{O}_{43}$, $\text{Bi}_{23}\text{P}_4\text{O}_{44.5}\text{-Bi}_{23}\text{As}_4\text{O}_{44.5}$, $\text{Bi}_{23}\text{P}_4\text{O}_{44.5}\text{-Bi}_{23}\text{V}_4\text{O}_{44.5}$, $\text{Bi}_{23}\text{As}_4\text{O}_{44.5}\text{-Bi}_{23}\text{V}_4\text{O}_{44.5}$, $\text{Bi}_{12}\text{P}_2\text{O}_{23}\text{-Bi}_{12}\text{As}_2\text{O}_{23}$, $\text{Bi}_{12}\text{P}_2\text{O}_{23}\text{-Bi}_{12}\text{V}_2\text{O}_{23}$, $\text{Bi}_{12}\text{As}_2\text{O}_{23}\text{-Bi}_{12}\text{V}_2\text{O}_{23}$ dan $\text{Bi}_7\text{AsO}_{13}\text{-Bi}_7\text{VO}_{13}$. Dalam sistem-sistem $\text{Bi}_7\text{PO}_{13}\text{-Bi}_7\text{AsO}_{13}$ dan $\text{Bi}_7\text{PO}_{13}\text{-Bi}_7\text{VO}_{13}$, dua fasa yang berlainan telah dikesan. Bahan-bahan berfasa tunggal yang dikaji merupakan konduktor ion oksida. Kekonduksian meningkat dengan penambahan kandungan vanadium, diikuti oleh arsenik dan fosforus. Di antara bahan-bahan yang disediakan, $\text{Bi}_{23}\text{V}_4\text{O}_{44.5}$ telah menunjukkan kekonduksian yang paling tinggi dengan $\sigma = 1.34 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ pada 300°C . Dalam usaha untuk meningkatkan kekonduksian, pendopan kimia dengan menggunakan PbO , $\text{Sr}(\text{NO}_3)_2$, Al_2O_3 , Ga_2O_3 , La_2O_3 , Fe_2O_3 dan sebagainya telah dilakukan pada bahan-bahan terpilih. Pepejal larutan yang terhad telah terhasil. Walau bagaimanapun, kekonduksian bahan-bahan terdop tersebut adalah kurang daripada bahan-bahan induk.

Selain daripada tindak balas keadaan pepejal, proses pengisaran bebola juga dijalankan dalam penyediaan $\text{Bi}_{23}\text{V}_4\text{O}_{44.5}$ dan $\text{Bi}_{14}\text{PO}_8$. Dalam proses pengisaran bebola, bahan yang berketumpatan tinggi, berserbuk halus dan bertaburan seragam telah dihasilkan, dan seterusnya membawa kepada peningkatan dalam kekonduksian dan pemalar dielektrik.

Kompoun sillenit dalam sistem $\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ dengan nisbah Bi:P berjulat antara 13:1 dan 16:1 telah disintesis dan larutan pepejal telah diperolehi dalam bahan-bahan tersebut. Penggantian P oleh V dalam $\text{Bi}_{14}\text{PO}_8$ menghasilkan larutan pepejal yang

terhad, sementara larutan pepejal yang lengkap telah diperolehi apabila P dalam $\text{Bi}_{14}\text{PO}_8$ digantikan oleh As. Peningkatan dalam kekonduksian telah diperhatikan dalam larutan pepejal yang didop dengan V. Pembentukan larutan pepejal yang terhad telah diperolehi apabila P digantikan oleh Pb^{2+} , Sr^{2+} , Al^{3+} , Ga^{3+} , Fe^{3+} , Si^{4+} , Ge^{4+} , dan Ti^{4+} . Kekonduksian bahan-bahan tersebut adalah lebih kurang sama dengan kompoun induk. Bahan-bahan tersebut merupakan konduktur ion oksida terutamanya pada suhu lebih daripada 800°C , di mana peralihan fasa $\gamma \rightarrow \delta'$ berlaku.

ACKNOWLEDGEMENTS

The author would like to express her deepest appreciation and gratitude to her dedicated supervisor, Prof. Dr. Lee Chnoong Kheng for her supervision, invaluable guidance, unfailing help, advice and suggestion throughout the course of this study. Thanks are also for her financial support at the early stage of the author's study. The author would also like to extend her special thanks to her co-supervisors, Prof. Dr. Abdul Halim Shaari, Dr. Chong Fai Kait, and Assoc. Prof. Dr. Taufiq Yap Yun Hin for their constant support, help and advice throughout her study.

The author is grateful to Prof. Dr. Mohd. Zobir Hussein and the Institute of Advanced Technology (ITMA) for the instrumental support in the density measurement and particle size analysis, respectively. The author is also grateful to all the technical staff especially Mr Kamal Margona and Mr Zulhisham Razali (DTA, TGA & DSC), Mdm Rusnani Amirudin and Mr Nordin Ismail (FT-IR), Mdm Susi (Raman) and Mdm Choo Chai Syam (ICP-AES) of Chemistry Department, Mdm Faridah Akmal Ismail, Ms Azilah Ab. Jalil and Mr Syabaris (SEM) of Institute Bioscience, UPM for their assistance, cooperation and helpful suggestion contributing towards the success of this study.

The author would also like to give her heart-felt thanks to Prof. Anthony R. West and Dr. Derek C. Sinclair for their guidance, patience and understanding during her research attachment at Department of Engineering Materials, University of Sheffield, UK in the

spring, 2002. Also not forgotten are friends in UK, especially Dr. Kirr, Gaby, Gillian, Tony, Mouldy, Tim, Antonio, Heath, Yam, Tik, Dong, Siao Wearn, Wei Wei, Leo and Sharon for their help when she was there.

The author is especially thankful to her husband W.M. Bon, for his love, devotion and understanding. Deepest affection is due to the author's beloved family and her parents-in-law for unconditional love and support. Sincere gratitude is extended to the author's labmates, friends, and housemates, in particular, Leng Tze, Poh Li, Chiu Sze, Han-fang, Sharon, Siew Teng, Pei Sin, Tien Ping, Amy and Chee Siong for the encouragement and suggestion.

Finally, her most profound thanks go to Ministry of Science, Technology and Environment (MOSTE), Malaysia for the financial support and the opportunity to be exposed to a world-class research centre at the University of Sheffield, UK from 9th April 2002 to 27th June 2002.



I certify that an Examination Committee met on 28th May 2004 to conduct the final examination of Lee Siew Ling on her Doctor of Philosophy thesis entitled "Preparation and Characterization of $\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$ (M=P, As, V) Oxide Ion Conductors" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

Tan Wee Tee, Ph.D.

Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairman)

Mohd. Zobir Hussein, Ph.D.

Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Zulkarnain bin Zainal, Ph.D.

Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Ibrahim Abu Talib, Ph.D.

Professor
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
(Independent Examiner)



GULAM RUSUL RAHMAT ALI, Ph.D.

Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 22 JUL 2004

This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as partial fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee are as follows:

Lee Chnoong Kheng, Ph.D.

Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairman)

Abdul Halim Shaari, Ph.D.

Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Chong Fai Kait, Ph.D.

Lecturer
Chemical Engineering Department
Universiti Teknologi Petronas
(Member)

Taufiq Yap Yun Hin, Ph.D.

Associate Professor
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
(Member)




AINI IDERIS, Ph.D.

Professor/Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: **16 AUG 2004**

DECLARATION

I hereby declare that the thesis is based on my original work except for the quotations and citation which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.



LEE SIEW LING

Date: 29/7/2004

TABLE OF CONTENTS

	Page
DEDICATION	ii
ABSTRACT	iii
ABSTRAK	vi
ACKNOWLEDGEMENTS	x
APPROVAL	xii
DECLARATION	xiv
LIST OF TABLES	xix
LIST OF FIGURES	xxiii
LIST OF ABBREVIATIONS AND SYMBOLS	xxxi

CHAPTER

1	INTRODUCTION	
1.1	Solid Electrolytes and Oxide Ion Conductors	1.1
1.1.1	Ionic Conduction	1.3
1.1.2	Solid Oxide Fuel Cell	1.5
1.1.3	Oxygen Sensors	1.8
1.2	Solid Solutions	1.9
1.3	Theory on Experimental Techniques	1.10
1.3.1	X-ray Diffraction (XRD)	1.10
1.3.2	Electrical Properties	1.13
	1.3.2.1 General Principles of the AC Method	1.14
	1.3.2.2 Feasible Application of AC Impedance Spectroscopy	1.17
	1.3.2.3 Cole-cole Plot	1.18
	1.3.2.4 Modulus Spectroscopy	1.26
1.3.3	Thermal Analysis	1.29
1.3.4	Scanning Electron Microscopy (SEM)	1.30
1.3.5	Fourier-transform Infrared (FT-IR) and Raman Spectroscopy	1.30
1.3.6	X-ray Photoelectron Spectroscopy (XPS)	1.31
1.4	Significance of Study	1.32
1.5	Objectives	1.33



2	LITERATURE REVIEW	
2.1	Bi ₂ O ₃ Oxide Ion Conductors	2.1
2.1.1	δ-Bi ₂ O ₃	2.2
2.1.2	γ-Bi ₂ O ₃	2.5
2.2	Bi ₂ O ₃ -P ₂ O ₅ Binary System	
2.2.1	Polymorphism and Phase Diagram	2.8
2.2.2	Synthesis	2.12
2.2.3	Crystal Structures	2.17
2.2.4	Electrical Properties	2.25
2.2.5	Introduction of Dopant	2.26
2.3	Bi ₂ O ₃ -As ₂ O ₅ Binary System	
2.3.1	Synthesis	2.30
2.3.2	Crystal Structures	2.31
2.3.3	Polymorphism and Conductivity	2.35
2.4	Bi ₂ O ₃ -V ₂ O ₅ Binary System	
2.4.1	Polymorphism and Phase Diagram	2.36
2.4.2	Synthesis	2.39
2.4.3	Crystal Structures	2.41
2.4.4	Electrical Properties	2.48
2.4.5	Introduction of Dopant	2.49
3	Experimental	
3.1	Sample Preparation	
3.1.1	Solid State Reaction with Manual Mixing	3.1
3.1.2	Solid State Reaction with Ball Milling Mixing	3.2
3.1.3	Bi ₂ O ₃ -P ₂ O ₅ Binary System	3.3
3.1.4	Bi ₂ O ₃ -As ₂ O ₅ Binary System	3.5
3.1.5	Bi ₂ O ₃ -V ₂ O ₅ Binary System	3.5
3.2	Pellet Preparation	3.6
3.3	Characterization	3.6
3.3.1	X-ray Diffraction (XRD)	3.7
3.3.2	Electrical Properties	3.8
3.3.3	Thermal Analysis	3.10
3.3.4	Scanning Electron Microscopy (SEM)	3.12
3.3.5	Fourier-transform Infrared (FT-IR) Spectroscopy	3.12
3.3.6	Raman Spectroscopy	3.12
3.3.7	Density Measurement	3.13
3.3.8	Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)	3.13
3.3.9	Particle Size Analysis	3.14
3.3.10	X-ray Photoelectron Spectroscopy (XPS)	3.15
3.4	Phase Diagram	3.15
3.4.1	Melting Point	3.16
3.4.2	Phase Stability	3.16
3.5	Estimation of Error	3.17

4	RESULTS AND DISCUSSION	
4.1	Bi ₂ O ₃ -P ₂ O ₅ Binary System	
4.1.1	Phase Purity	4.1
4.1.2	Density Measurement	4.13
4.1.3	Element Determination	4.15
4.1.4	Electrical Properties	4.16
4.1.5	Thermal Analysis	4.30
4.1.6	Fourier-transform Infrared (FT-IR) and Raman Spectroscopy	4.32
4.2	Bi ₂ O ₃ -As ₂ O ₅ Binary System	
4.2.1	Phase Purity	4.39
4.2.2	Density Measurement	4.48
4.2.3	Element Determination	4.49
4.2.4	Electrical Properties	4.50
4.2.5	Thermal Analysis	4.57
4.2.6	Fourier-transform Infrared (FT-IR) and Raman Spectroscopy	4.60
4.3	Bi ₂ O ₃ -V ₂ O ₅ Binary System	
4.3.1	Phase Purity	4.65
4.3.2	Density Measurement	4.74
4.3.3	Element Determination	4.76
4.3.4	Electrical Properties	4.77
4.3.5	Thermal Analysis	4.97
4.3.6	Fourier-transform Infrared (FT-IR)	4.100
4.4	xBi ₂ O ₃ : (P/As/V) ₂ O ₅ Solid Solutions, $x = 5.5, 5.75, 6, 7$	
4.4.1	Formation of Solid Solutions	4.102
4.4.2	Density Measurement	4.117
4.4.3	Electrical Properties	4.120
4.4.4	Thermal Analysis	4.125
4.4.5	Fourier-transform Infrared (FT-IR)	4.133
4.4.6	Introduction of Dopants	
4.4.6.1	Phase Purity	4.136
4.4.6.2	Electrical Properties	4.143
4.5	Sillenite and other Materials in Cubic Systems	
4.5.1	Phase Purity	4.148
4.5.2	Density Measurement	4.155
4.5.3	Elemental Determination	4.160
4.5.4	Electrical Properties	4.161
4.5.5	Thermal Analysis	4.182
4.5.6	Fourier-transform Infrared (FT-IR)	4.185
4.6	Bi ₁₄ P _{1-x} M _x O ₈ Solid Solutions	
4.6.1	Formation of Solid Solutions	4.188
4.6.2	Density Measurement	4.202
4.6.3	Electrical Properties	4.204
4.6.4	Thermal Analysis	4.209
4.6.5	Fourier-transform Infrared (FT-IR)	4.214

5	CONCLUSION	5.1
	REFERENCES	R.1
	APPENDICES	A.1
	BIODATA OF THE AUTHOR	B.1
	LIST OF PUBLICATIONS AND CONFERENCES/SEMINARS ATTENDED	C.1



LIST OF TABLES

Table		Page
1.1	Equation for real axis intercepts in all four formalisms for three equivalent circuit in Figure 1.7	1.21
1.2	Capacitance values and their possible interpretation (Sinclair <i>et al.</i> , 2000)	1.23
2.1	Conductivities of different phases of Bi_2O_3 measured between platinum electrodes	2.1
2.2	List of elements doped in $\delta\text{-Bi}_2\text{O}_3$	2.4
2.3	Synthesis conditions of Bi-rich compounds in $\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ binary system	2.13
2.4	Structural data of compounds in $\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ binary system, in the concentration range 50-85 mol% P_2O_5	2.18
2.5	Structural data of P-rich compounds in $\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ binary system	2.24
2.6	Synthesis conditions of compounds in $\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ binary system via solid solution reaction	2.40
2.7	Structural data of compounds in $\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ binary system	2.41
2.8	Some characteristics of quenched films of $\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ (Sekiya <i>et al.</i> , 1985)	2.47
2.9	List of elements doped in $\text{Bi}_4\text{V}_2\text{O}_{11}$	2.50
3.1	Synthesis temperature of materials in $x\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ binary system	3.4
3.2	Wavelength of elements used and concentration of standard solutions prepared in ICP-AES analysis	3.14
3.3	Estimation of error for experimental parameters	3.17
4.1	The lattice parameters of $x\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$, $5.5 \leq x \leq 6$ solid solutions from X-ray diffraction data	4.6
4.2	Weight loss in sample where $\text{Bi/P} = 6.25$ and 6.5 in prolong heating treatment at 900°C	4.8



4.3	The lattice parameters of $x\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ binary system, $x = 7$ and 7.25 from X-ray diffraction data	4.10
4.4	Summary of $x\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ binary system, $5 \leq x \leq 9$	4.11
4.5	Densities of $x\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ binary system, $5.5 \leq x \leq 7.25$	4.13
4.6	Densities calculated from XRD results for $x\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ binary system, $5.5 \leq x \leq 6$	4.15
4.7	Elemental composition of materials in $x\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ binary system, $5 \leq x \leq 7$	4.16
4.8	Conductivity (σ_{300} and σ_{600}) and activation energy (E_a) of $x\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ binary system, $5.5 \leq x \leq 7.25$	4.22
4.9	Raman band position of $\text{Bi}_{23}\text{P}_4\text{O}_{44.5}$	4.36
4.10	The lattice parameters of $x\text{Bi}_2\text{O}_3\text{-As}_2\text{O}_5$ binary system from X-ray diffraction data	4.45
4.11	Densities of $x\text{Bi}_2\text{O}_3\text{-As}_2\text{O}_5$ binary system, $5 \leq x \leq 7$	4.48
4.12	Elemental composition of materials in $x\text{Bi}_2\text{O}_3\text{-As}_2\text{O}_5$ binary system, $5 \leq x \leq 7$	4.49
4.13	Conductivity (σ_{300} and σ_{600}) and activation energy (E_a) of $x\text{Bi}_2\text{O}_3\text{-As}_2\text{O}_5$, $5 \leq x \leq 7$	4.53
4.14	The lattice parameters of $x\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$, $5 \leq x \leq 7$ solid solutions from X-ray diffraction data	4.71
4.15	Densities of $x\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ binary system, $5 \leq x \leq 7$	4.75
4.16	Elemental composition of materials in $x\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ binary system, $5 \leq x \leq 7$	4.76
4.17	Particle size of $\text{Bi}_{23}\text{V}_4\text{O}_{44.5}$ prepared via solid state reaction with manual mixing and ball mill (bm) mixing	4.82
4.18	Capacitance and the relative permittivity at Z''_{max} of $\text{Bi}_{23}\text{V}_4\text{O}_{44.5}$ taken in the 1 st cooling cycle	4.85
4.19	Conductivity (σ_{300} and σ_{600}) and activation energy (E_a) of $x\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ binary system, $5 \leq x \leq 7$	4.91

4.20	Lattice parameters of $5.5\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$, $\text{M} = \text{P, As, V}$ solid solutions from X-ray diffraction data	4.113
4.21	Lattice parameters of $5.75\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$, $\text{M} = \text{P, As, V}$ solid solutions from X-ray diffraction data	4.114
4.22	Lattice parameters of $6\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$, $\text{M} = \text{P, As, V}$ solid solutions from X-ray diffraction data	4.115
4.23	Lattice parameters of $7\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$, $\text{M} = \text{P, As, V}$ solid solutions from X-ray diffraction data	4.116
4.24	Densities of $\text{Bi}_{22}\text{P}_{4-4x}\text{As}_{4x}\text{O}_{43}$ solid solutions	4.118
4.25	Densities of $\text{Bi}_{22}\text{P}_{4-4x}\text{V}_{4x}\text{O}_{43}$ solid solutions	4.118
4.26	Densities of $\text{Bi}_{22}\text{As}_{4-4x}\text{V}_{4x}\text{O}_{43}$ solid solutions	4.119
4.27	Conductivity (σ_{300} and σ_{600}) and activation energy (E_a) of $x\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$, $\text{M} = \text{P, As, V}$ and related materials	4.124
4.28	Phase purity of the doped materials in $5.75\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$, $\text{M} = \text{P, As, V}$	4.138
4.29	Conductivity (σ_{300} and σ_{600}) and activation energy (E_a) of $5.75\text{Bi}_2\text{O}_3\text{-M}_2\text{O}_5$, $\text{M} = \text{P, V, As}$ and related materials	4.146
4.30	Phases synthesized in $x\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ binary system, $10 \leq x \leq 25$	4.150
4.31	The lattice parameters of sillenite materials from X-ray diffraction Data	4.154
4.32	Densities of Bi_xPO_8 , $13 \leq x \leq 16$	4.157
4.33	Densities calculated from XRD results for Bi_xPO_8 , $13 \leq x \leq 16$	4.159
4.34	Elemental composition of materials Bi_xPO_8 , $13 \leq x \leq 16$	4.160
4.35	Conductivity values of $\text{Bi}_{14}\text{PO}_8$ and related materials at 500°C and 800°C	4.168

4.36	Particle size of $\text{Bi}_{14}\text{PO}_8$ prepared via solid state reaction with manual mixing and ball mill (bm) mixing	4.172
4.37	Capacitance and the relative permittivity at Z''_{max} of $\text{Bi}_{14}\text{PO}_8$ taken at the 1 st cooling cycle	4.179
4.38	DTA results of sillenite materials in Bi_2O_3 - P_2O_5 binary system	4.182
4.39	Results of doping experiments on $\text{Bi}_{14}\text{PO}_8$ ($\text{Bi}_{14}\text{P}_{1-x}\text{M}_x\text{O}_8$)	4.188
4.40	The lattice parameters of $\text{Bi}_{14}\text{P}_{1-x}\text{As}_x\text{O}_8$ from X-ray diffraction data	4.191
4.41	Lattice parameters of $\text{Bi}_{14}\text{P}_{1-x}\text{V}_x\text{O}_8$ from X-ray diffraction data	4.196
4.42	Densities of $\text{Bi}_{14}\text{P}_{1-x}\text{As}_x\text{O}_8$ solid solutions	4.203
4.43	Densities of $\text{Bi}_{14}\text{P}_{1-x}\text{V}_x\text{O}_8$, $0 \leq x \leq 0.3$, solid solutions	4.203
4.44	Conductivity values of $\text{Bi}_{14}\text{AsO}_8$ and $\text{Bi}_{14.3}\text{AsO}_8$ (6.52 mol% As_2O_5) at 500°C	4.207
4.45	Conductivity values of $\text{Bi}_{14}\text{PO}_8$ and doped materials at 500°C and 800°C	4.209
4.46	DTA results of $\text{Bi}_{14}\text{P}_{1-x}\text{V}_x\text{O}_8$ solid solutions	4.213
4.47	DTA results of $\text{Bi}_{14}\text{P}_{1-x}\text{M}_x\text{O}_8$ solid solutions	4.214

LIST OF FIGURES

Figures	Page
1.1 Electrical conductivities of selected common substances and representative solid electrolytes (Greenblatt, 1994)	1.2
1.2 Concept diagram of SOFC (Fisher, 1999)	1.7
1.3 Principle of X-ray diffraction	1.12
1.4 Admittance bridge	1.15
1.5 Impedance bridge	1.15
1.6 Semi-circle and spike in a complex Z^* plot	1.19
1.7 Possible equivalent circuits and its corresponding frequency response in complex plane plots for the four electrical formalisms (Hirose and West, 1996)	1.20
1.8 Brickwork model of grain boundary regions in a ceramic placed between metal electrodes (Irvine <i>et al.</i> , 1990)	1.22
1.9 Equivalent circuit for a polycrystalline solid electrolyte: C_{dl} -electrode double-layer capacitance; C_b , R_b – bulk crystals; C_{gb} , R_{gb} —grain boundaries	1.24
1.10 Impedance diagram due to a blocking interface: (a) a perfectly smooth interface; (b) rough electrode or due to Warburg impedance (Armstrong and Todd, 1995)	1.25
1.11 The Z'' and M'' spectroscopic plots respective to a complex Z^* plot in Figure 1.7	1.29
2.1 Structure models for δ - Bi_2O_3 ; (a) Sillén model showing ordered defects in $\langle 111 \rangle$ direction; (b) Gattow model: average distribution of 6 oxygen atoms about the sites of $Fm3m$	2.3
2.2 Outline of one unit cell of $\text{Bi}_{12}\text{PbO}_{19}$ in the sillenite phase showing the tetrahedra around each (2a) site cation and the O(2) and O(3) positions	2.8
2.3 Equilibrium diagram of the Bi_2O_3 - P_2O_5 system (Volkov <i>et al.</i> , 1983)	2.9



2.4	Bi ₂ O ₃ -P ₂ O ₅ phase diagram in the concentration range 50-85 mol% P ₂ O ₅ (Voevodskii <i>et al.</i> , 1997)	2.12
2.5	Structure and cell relations of tetragonal Bi ₂ O ₂ layers, with O ²⁻ in the layer plane and Bi ³⁺ above and below, respectively (Jie and Eysel, 1995)	2.22
2.6	Distances in the coordination polyhedron of Bismuth. Standard deviation ≤ 0.010 Å (Palkina and Jost, 1975)	2.25
2.7	Planes of monoclinic lattice parameter of unlimited ternary solid solution in the system Bi ₁₂ P ₂ O ₂₃ -Bi ₁₂ As ₂ O ₂₃ -Bi ₁₂ V ₂ O ₂₃ (Jie and Eysel, 1995)	2.29
2.8	A view of the structure of α-BiAsO ₄ (Bedlivy and Mereiter, 1982)	2.32
2.9	Phase transition of Bi ₄ V ₂ O ₁₁ (Abraham <i>et al.</i> , 1988)	2.37
2.10	Bi ₂ O ₃ -V ₂ O ₅ phase diagram over the composition range 0-15 mol% V ₂ O ₅ (Kargin and Voevodskii, 1997)	2.38
3.1	Flow chart for the synthesis process of samples	3.2
3.2	Flow chart of methodology	3.7
4.1	XRD patterns of xBi ₂ O ₃ -P ₂ O ₅ , 5 ≤ x ≤ 9: (a) x = 5, (b) x = 5.25, (c) x = 5.5, (d) x = 5.75, (e) x = 6, (f) x = 6.25, (g) x = 6.5, (h) x = 6.75, (i) x = 7, (j) x = 7.25, (k) x = 7.5, (l) x = 8, (m) x = 8.5, (n) x = 9	4.2
4.2	Comparison of XRD pattern with ICDD using μPDSM: (a) 5Bi ₂ O ₃ -P ₂ O ₅ and (b) ICDD card number 26-220	4.3
4.3	XRD pattern of Bi ₂₃ P ₄ O _{44.5}	4.5
4.4	XRD pattern of Bi ₇ PO ₁₃	4.9
4.5	Comparison of XRD pattern with ICDD using μPDSM: (a) 9Bi ₂ O ₃ -P ₂ O ₅ and (b) δ-Bi ₂ O ₃ (ICDD card number 27-52)	4.12
4.6	Complex impedance plane plot for Bi ₂₃ P ₄ O _{44.5} at (a) 300°C, (b) 500°C	4.17
4.7	A combined Z'' and M'' spectroscopic plots for Bi ₂₃ P ₄ O _{44.5} at 300°C	4.20
4.8	Arrhenius plots of xBi ₂ O ₃ -P ₂ O ₅ binary system, 5.5 ≤ x ≤ 7.25	4.21